# Early 20th C Russian Painting? Raman Identification of Modern Pigments on a Pastel supposedly Painted by the Renowned Artist Natalia Goncharova

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## Abstract
A pastel painting considered to have been painted by Natalia Goncharova in 1913/14 has been shown by Raman identification of key pigments to have been painted in or after 1952. The implications of this discovery, based on Raman microscopy, are discussed. The present investigation of a small painting of this type (Figure 1.) reveals that it could not have been painted around 1913/1914 as believed prior to this investigation, but in the period 1952 (when the pigment dioxazine was first synthesised) to 1962 (if painted by Goncharova, as this is the year in which she died). This result highlights the need for reliable and perceptive dating procedures for valuation purposes.

## KEYWORDS
Goncharova, pigment identification, oil pastel

## Introduction
Natalia Goncharova (1881-1962) was a leading artist of the Russian avant-garde movement during the early 20$^{th}$ century. Having originally trained as a sculptor, Goncharova turned to painting c.1902 and, along with fellow artist Mikhail Larionov (1881-1964) who was to become her lifelong companion, she developed a highly colourful painting technique in a variety of styles that included impressionism, neo-primitivism, cubism, rayism and futurism. During her early career, Goncharova exhibited her paintings widely in Russia and later in Paris, Spain, Rome, London, Tokyo and New York, later making Paris her long term home (from c. 1919 onwards). She was prolific painter, continuing to paint into the late 1950s despite the onset of crippling arthritis; she died in Paris in 1962. In the west Goncharova was, until recently, known more widely for her set and costume design, working with Sergei Diaghilev, director of the Ballets Russes (Russian Ballet).[1,2] However, renewed interest in her paintings has resulted in sales exceeding $10 million, making Goncharova (in 2010) the most expensive female artist at auction.

In 1912, Goncharova and Larionov developed the new style of abstract painting which they termed Rayism (Luchizm; sometimes termed Rayonism), based on the depiction of light rays emanating from objects and their intersection.[1,2] The early Rayist phase was reportedly short-lived, superceded by the development of neo-primitivism and cubo-futurism styles and the increasing importance of Goncharova's set and costume design work.[1] However, during the 1950s Goncharova is known to

have produced a limited number of Rayist paintings and drawing for an exhibition at the Galerie de l'Institut in 1956.[1,2,3] Goncharova rarely dated her paintings on execution and signed only few of them; her signature where present, varies between simple initials in either Cyrillic or western alphabet, or with her full surname included, as "N.Goncharova" or "N. Gontcharova" to incorporate western interpretation of the Russian spelling.

The palette of the Russian avant-garde painters has been the subject of only limited scientific study.[4] Here we present a Raman study of a pastel painting in private ownership, signed "N. Gontcharova" in black ink in the lower left corner and ascribed a date of c.1913 (Fig. 1). The untitled work measures 13.5 cm x 21.5 cm and is executed on a brown paper substrate in the Rayist style; it is richly coloured using a range of purple, yellow, orange, blue, green, red and white pigments, with individual areas bordered with bold black lines; no evidence for any restoration or overpaint is present. The investigation was greatly assisted by easy access to libraries of Raman spectra of pigments and dyes[5-8].

## Experimental

### Instrumentation

Raman spectra of the pigments were collected using two different Renishaw Raman microscope systems (a RM1000 and an InVia), each equipped with an 1800 lines/mm grating, a holographic notch filter, a thermoelectrically-cooled charge coupled device (CCD) detector, and a Leica DM microscope. A He/Ne laser provided exciting radiation at 632.8 nm and an Ar ion laser provided exciting radiation at 514.5 nm, with a laser power at the sample of about 0.4-0.8 mW. Spectra were recorded in the range 2500-100 $cm^{-1}$ by collecting 20 scans with an exposure time of 10 s each, and an estimated spectral resolution of 1 $cm^{-1}$.

Fourier transform infrared (FTIR) spectra were collected by pressing the paint sample directly onto the central area of the diamond window of a Bruker Opus Fourier transform Infra-red spectrometer. The spectra were recorded in the range from 4000 to 380 $cm^{-1}$, using 24 scans at a resolution of 4 $cm^{-1}$. The background scan was automatically subtracted and the scans averaged to produce a spectrum.

## Results and Discussion

Raman spectra were collected from 6-10 locations in each of the main areas of colour on the painting. The pigments identified are: titanium dioxide white (rutile-type, $TiO_2$), zinc white (ZnO), barium white ($BaSO_4$), phthalocyanine blue ($CuC_{32}H_{16}N_8$), phthalocyanine green ($CuC_{32}H_{15}ClN_8$), hematite ($Fe_2O_3$), dioxazine purple ($C_{32}H_{18}C_{l2}N_4O_2$), pyrazolone orange ($C_{32}H_{24}Cl_2N_8O_2$) and carbon-based black (Table 1 and Figs. 2-3). Although carbon-based black and hematite-based pigments such as red ochre are amongst the earliest materials used by artists[9,10], five of the pigments identified were first synthesised during or after the 1930s. Whilst phthalocyanine blue and green pigments and the pyrazolone orange pigment identified here (Pigment Orange 13) have been commercially available since the mid-1930s[11], it is the identification of titanium dioxide, rutile-type and particularly violet dioxazine that are the most significant. The synthetic form of rutile has been manufactured since c.1947,[12] with the polycyclic pigment dioxazine commercially available from 1952.[13]

The results therefore indicate that the earliest year in which this painting could have been executed is 1952.

Further, FTIR analysis of a microscopic sample of red pigment from an area of red paint towards the centre of the painting shows that it contains an oil, in addition to hematite and clay (which together may represent natural ochre) and some calcium carbonate (Fig. 4). Pastels, which consist of powdered pigment and a binder, have been in use since c.15$^{th}$ century. They were historically manufactured using natural gums such as gum Arabic and gum tragacanth, often with some chalk or gypsum added. While oil/wax 'paint sticks' were reported to have been invented in 1902[14] and have been found on an early 20th century work by a Norwegian Artist[15]; Oil pastels, those with an oil binder, were developed in the mid-1920s
, becoming widely available in Europe in the 1930s. However, it is reported that they were difficult to obtain during World War II until French manufacturers developed a fine art version for professional artists in 1949.[16,17] This appears to be further evidence that the painting was not executed until the 1950s at the earliest.

## Conclusions

The palette used for the pastel painting has been established to consist of the following nine pigments: titanium dioxide white (rutile-type), zinc white, barium white, carbon-based black, phthalocyanine blue and green, hematite, pyrazolone orange (Pigment Orange 13) and dioxazine purple (Pigment Violet 23). The identification of this form of dioxazine purple, first commercially available from c. 1952, indicates that the painting could not have been executed before this date. The pastel paints have been applied in thin layers over the paper substrate, with paper fibres visible through the painted surface; there is no apparent retouching or overpainting evident, indicating that it is the original surface that has been examined here. Further, the use of oil as the binding medium in the pastel also indicates an execution date of post-c.1950. The original date given to the painting as c.1913 is therefore incorrect and thus the painting cannot belong to Goncharova's main period of Rayism (c.1912-1925). Although Goncharova is known to have produced some new Rayist paintings and drawings during the 1950s for her exhibition at the Galerie de l'Institut, Paris in 1956, there exists only a narrow window in which the painting could have been executed (1952 until her death in 1962), a period during which she became increasingly afflicted seriously with arthritis. It therefore seems highly unlikely that this painting is her work.

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**Figure captions**

**Figure 1.** The small pastel painting under study which measures 13.5 cm x 21.5 cm.

**Figure 2.** Raman spectra of (a) carbon black; (b) hematite; (c) barium white; (d) zinc white; and (e) rutile.

**Figure 3.** Raman spectra of (a) pyrazolone; (b) copper phthalocyanine blue; (c) copper phthalocyanine green; and (d) dioxazine.

**Figure 4.** FTIR spectrum obtained from a sample of the red paint (taken from towards the centre of the painting, 4.5 cm down from the top edge and 7.5 cm inwards from the proper right side), with bands at 2918, 2870, 1730, 1151 and 1098 $cm^{-1}$ characteristic of an oil; the bands at 520 and 452 $cm^{-1}$ indicate the presence of hematite ($\alpha$-$Fe_2O_3$), with the bands at 1418, 874 and 712 $cm^{-1}$ indicative of calcium carbonate ($CaCO_3$) and the bands at 3694, 3618, 1027, 913, 530 and 390 attributal to kaolinite (clay).

**Table 1.** Pigments identified on the painting and their date of first availablity

| *Pigment Identified* | | *Year first marketed as a pigment* | *Location* |
|---|---|---|---|
| 1 | Carbon-based black (carbon) | antiquity[9] | All black areas tested, including signature |
| 2 | Iron(III)oxide - hematite | antiquity[10] | Reds throughout |
| 3 | Barium white (barium sulfate) | early 19th century[18] | Minor amounts throughout the whites |
| 4 | Zinc white (zinc oxide) | 1834[19] | Large white areas near centre |
| 5 | Phthalocyanine blue (copper phthalocyanine) | 1936[11] | Blues throughout |
| 6 | Phthalocyanine green (copper phthalocyanine) | 1938[11] | Greens throughout |
| 7 | Disazo pigment (pyrazolone) Pigment Orange 13 | 1930s[11] | Yellow/orange/brown shades |
| 8 | Titanium dioxide white (rutile) | 1947[12] | Whites near top and bottom edges |
| 9 | Polycyclic pigment (dioxazine) Pigment Violet 23 | Post-1952[13] | Purples throughout |